

## METHOD 7471A

### MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

#### 2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

#### 3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

#### 4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M KMnO<sub>4</sub> and 10% H<sub>2</sub>SO<sub>4</sub>, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

## 5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO<sub>3</sub>.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

## 7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as Cl<sub>2</sub> could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H<sub>2</sub>SO<sub>4</sub> and 2 mL of concentrated HNO<sub>3</sub> are added to the 0.2 g of sample. Add 5 mL of saturated KMnO<sub>4</sub> solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of KMnO<sub>4</sub> solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

## 8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

## 9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

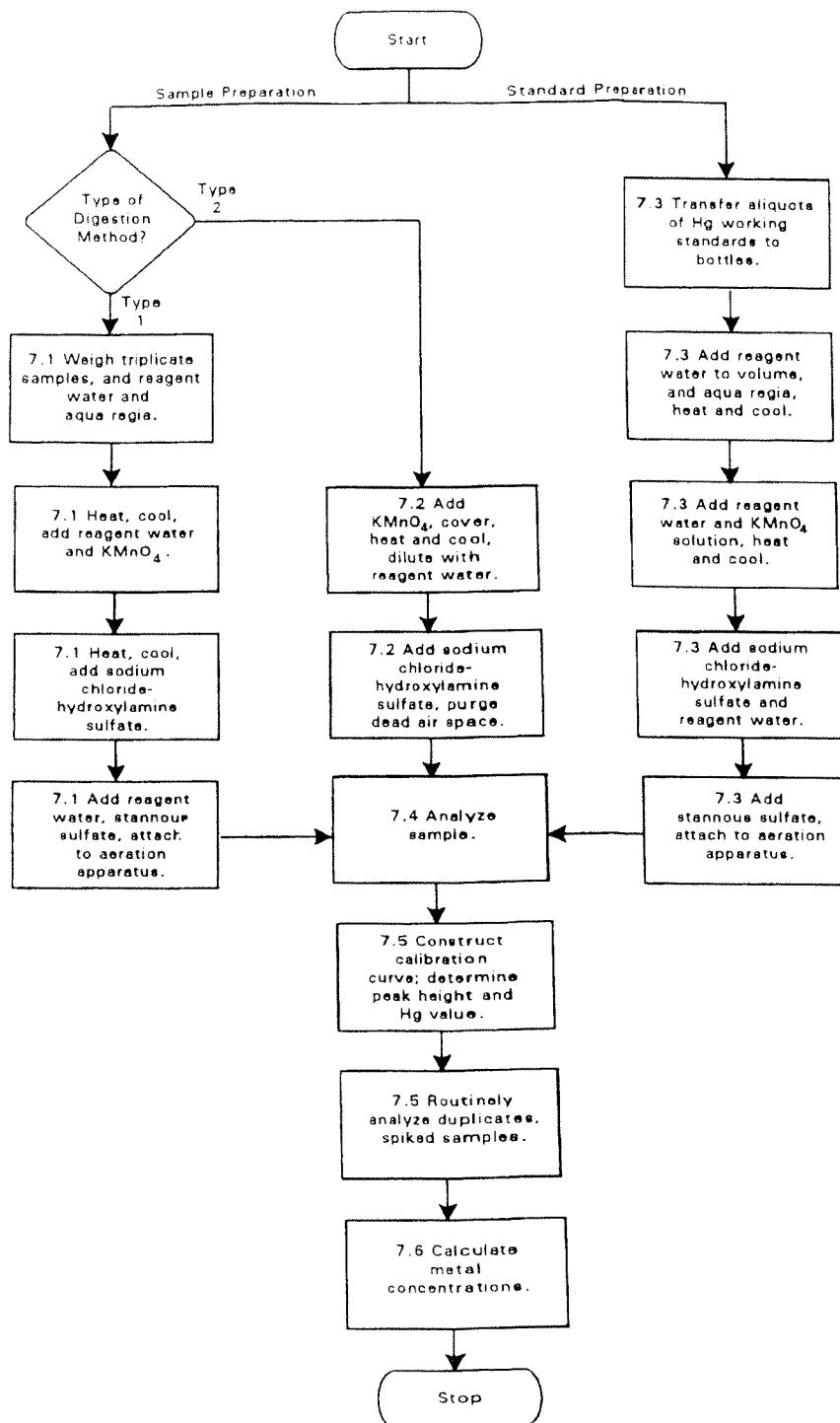
## 10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

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MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)





HALOGENATED AND AROMATIC VOLATILE ORGANIC COMPOUNDS (VOCs) BY GAS CHROMATOGRAPHY

SW-846 Methods 8010A and 8020A or Method 8021A

Table 1A. Summary of Holding Times and Preservation for Halogenated and Aromatic Volatile Organic Compounds by Gas Chromatography

Analytical Parameter <sup>a</sup>	Technical and Contract Holding Times	Preservation
Volatile Organic Compounds (VOCs) in Water	<u>Technical</u> : 7 days from collection; <u>Contract</u> : 5 days from receipt at laboratory	Cool to 4EC ±2EC;
VOCs in Water	<u>Technical</u> : 14 days from collection; <u>Contract</u> : 10 days from receipt at laboratory	HCl to pH <2; Cool to 4EC ±2EC
VOCs in Soil	<u>Technical</u> : 48 hours <u>Contract</u> : 48 hours	Cool to 4EC ±2EC; sealed zero headspace containers; freezing can extend the holding time <sup>b</sup>
VOCs in Soil	<u>Technical</u> : 14 days from collection; <u>Contract</u> : 10 days from receipt at laboratory	Preserved samples: in methanol <sup>c</sup> or sodium bisulfate <sup>d</sup>

<sup>a</sup> Individual target compounds are listed in Tables 1B and 1C.

<sup>b</sup> Freezing the sample can extend the holding time; however, 48 hours unfrozen holding time will be considered cumulative.

<sup>c</sup> Use Method 5030 for purge and trap.

<sup>d</sup> Use Method 5035 for purge and trap.

pH of each sample must be recorded and reported with sample results.

**Data Calculations and Reporting Units:**

Calculate the calibration factors (CFs) and the concentration of individual analytes according to the equations specified in Sections 7.4.2 and 7.10.1, respectively, of Method 8000B. Report water sample results in concentration units of micrograms per liter (Fg/L). Report soil sample results on a dry-weight basis in micrograms per kilogram (Fg/kg). Report percent solid and percent moisture to the nearest whole percentage point.

For rounding results, adhere to the following rules:

- If the number following those to be retained is less than 5, round down;
- If the number following those to be retained is greater than 5, round up; or
- If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

Table 1B. Target Compound List, CAS Numbers, and Contract Required Quantitation Limits for Halogenated Volatile Organic Compounds by Gas Chromatography

SW-846 Method 8010A or 8021A

<u>Compound</u>	<u>CAS Number</u>	<u>CRQL</u> ( $\mu\text{g/L}$ or $\mu\text{g/kg}$ )
Benzyl chloride	100-44-7	1
Bromobenzene	108-86-1	1
Bromodichloromethane	75-27-4	1
Bromoform	75-25-2	1
Bromomethane	74-83-9	1
Carbon tetrachloride	56-23-5	1
Chloroethane	75-00-3	1
2-Chloroethylvinylether	110-75-8	1
Chloroform	67-66-3	1
Chloromethane	74-87-3	1
Dibromochloromethane	124-48-1	1
Dibromomethane	74-95-3	1
Dichlorodifluoromethane	75-71-8	1
1,1-Dichloroethane	75-34-3	1
1,2-Dichloroethane	107-06-2	1
1,1-Dichloroethene	75-35-4	1
trans-1,2-Dichloroethene	156-60-5	1
1,2-Dichloropropane	78-87-5	1
cis-1,3-Dichloropropene	10061-01-5	1
trans-1,3-Dichloropropene	10061-02-6	1
Methylene chloride	75-09-2	5
1,1,2,2-Tetrachloroethane	79-34-5	1
1,1,1,2-Tetrachloroethane	630-20-6	1
Tetrachloroethene	127-18-4	1
1,1,1-Trichloroethane	71-55-6	1
1,1,2-Trichloroethane	79-00-5	1
Trichloroethene	79-01-6	1

Trichlorofluoromethane	75-69-4	1
1, 2, 3-Trichloropropane	96-18-4	1
Vinyl chloride	75-01-4	1
<hr/>		
<b>Additional Compounds:</b>		
1, 2-Dibromo-3-chloropropane	96-12-8	1
1, 2-Dibromoethane	106-93-4	1
1, 3-Dichloropropane	142-28-9	1
Dichlorofluoromethane	75-43-4	1

Table 1C. Target Compound List, CAS Numbers, and Contract Required Quantitation Limits for Aromatic Volatile Organic Compounds by Gas Chromatography

SW-846 Method 8020A or 8021A

<u>Compound</u>	<u>CAS Number</u>	<u>CRQL</u> <u>(µg/L or µg/kg)</u>
Benzene	71-43-2	1
Chlorobenzene	108-90-7	1
1, 2-Dichlorobenzene	95-50-1	1
1, 3-Dichlorobenzene	541-73-1	1
1, 4-Dichlorobenzene	106-46-7	1
Ethylbenzene	100-41-4	1
Toluene	108-88-3	1
Xylenes (Total)	1330-20-7	1

**Table 2. Summary of Calibration Procedures for Halogenated and Aromatic volatile Organic Compounds by Gas Chromatography**

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points for each analyte) (ICAL) <sup>a, b, c</sup>	Initially; whenever required, due to failure of CCV	RSD for CFs $\leq 30\%$ ; or, correlation coefficient ( $r$ ) of linear regression $\geq 0.99$	1. Terminate analysis 2. Recalibrate and verify before sample analysis
Continuing Calibration Verification (CCV)	Daily, every 12-hour, every ten samples, and end of run	%D between CF of CCV and avg CFs from ICAL $<\pm 25\%$	1. Recalibrate and verify 2. Reanalyze samples back to last good CCV
Retention time evaluation of CCV standards	Each analysis of CCV standard	$\pm 3 \times$ the SD of the avg ICAL RT for each analyte	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV

<sup>a</sup> The ICAL low standard must be above but near the CRQL. The low ICAL standard must have a signal to noise ratio  $\geq 5:1$ . If this requirement cannot be met, the laboratory must submit a MDL study as part of the data package.

<sup>b</sup> ICAL and continuing CAL standards must contain all target analytes listed in Table 1B.

<sup>c</sup> Report the retention time window for each analyte. Determine retention time windows as  $\pm 3 \times$  the standard deviation of the average initial calibration retention time for each analyte.

**Table 3. Summary of Internal Quality Control Procedures for Halogenated and Aromatic Volatile Organic Compounds by Gas Chromatography**

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Each 12-hour time period, minimum of one per SDG <sup>a</sup>	< CRQL for each compound	1. Investigate the source of contamination and document. 2. Reanalyze all samples processed with a blank that is out of control.
Instrument Blank	After any sample which contains a target compound concentration >50 ppb	< CRQL for each compound	1. Investigate the source of the problem and document. 2. Acceptance criterion must be met before proceeding with further analysis, in order to demonstrate that there is no analyte carryover.
Surrogate Spikes <sup>b</sup>	Every sample, standard and method blank	Water Sample: 75-125% of expected value; Soil Sample: 65-135% of expected value	1. Reanalyze all samples with non-compliant surrogate recoveries
Matrix Spike and Matrix Spike Duplicate (MS/MSD) <sup>c</sup>	One MS/MSD set per batch or SDG (1 MS/MSD set per 20 samples minimum)	Water Sample: 75-125% of expected value; Soil Sample: 65-135% of expected value;	#30% RPD between MS and MSD 1. Report in case narrative

<sup>a</sup> SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.  
<sup>b</sup> Surrogates: Halogenated compounds - 50 ng of one of the following three compounds: bromochlormethane, 2-bromo-1-chloropropane, or 1,4-dichlorobutane.  
<sup>c</sup> Aromatic compounds - 50 ng of one of the following two compounds: 1,1,1-trifluorotoluene and 4-bromofluorobenzene (BFB).

c Spike MS/MSD with 10 ppb of the following halogenated and aromatic VOCs: 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene.

Dilute and reanalyze samples which contain one or more target analytes at concentrations above the initial calibration range. Results for such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

Second column confirmation is required for all positive results. Confirmation must be performed on a column of a phase different from that used for quantitation. Confirmation analyses must meet all calibration criteria specified in Table 2 and blank acceptance criteria specified in Table 3.



**TOTAL PETROLEUM HYDROCARBONS (TPH) as Gasoline and Diesel**

SW-846 Method 8015B (Revision 2, December 1996)

**Table 1A. Summary of Contract Required Quantitation Limits, Holding Times, and Preservation for Total Petroleum Hydrocarbons (TPH) as Gasoline and Diesel**

Analytical Parameter <sup>a</sup>	Technical and Contract Holding Times	Preservation
Total Petroleum Hydrocarbons (TPH) as Gasoline in Water Samples	<u>Technical</u> : 7 days from collection; <u>Contract</u> : 5 days from receipt at laboratory	Cool to 4EC ±2EC
TPH as Gasoline in Water Samples	<u>Technical</u> : 14 days from collection; <u>Contract</u> : 10 days from receipt at laboratory	HCl or H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool to 4EC ±2EC
TPH as Gasoline in Soil Samples	<u>Technical</u> : 48 hours <u>Contract</u> : 48 hours	Cool to 4EC ±2EC; sealed zero headspace containers; freezing can extend the holding time <sup>b,c</sup>
TPH as Gasoline in Soil Samples	<u>Technical</u> : 14 days from collection; <u>Contract</u> : 10 days from receipt at laboratory	Preserved samples: in methanol <sup>d</sup> or sodium bisulfate <sup>e</sup>
TPH as Diesel in Water Samples	<u>Technical to Extraction</u> : 14 days from collection; <u>Contract to Extraction</u> : 10 days from receipt at laboratory <u>Technical and Contract to Analysis</u> : 40 days from extraction	Cool to 4EC ±2EC; HCl or H <sub>2</sub> SO <sub>4</sub> to pH<2 <sup>f</sup>
TPH as Diesel in Soil Samples	<u>Technical to Extraction</u> : 14 days from collection; <u>Contract to Extraction</u> : 10 days from receipt at laboratory <u>Technical and Contract to Analysis</u> : 40 days from extraction	Cool to 4EC ±2EC

<sup>a</sup> Individual target compounds are listed in Table 1B.

<sup>b</sup> Freezing the sample can extend the holding time; however, 48 hours unfrozen holding time will be considered cumulative.

<sup>c</sup> Use Method 5021 for headspace analysis.

<sup>d</sup> Use Method 5030 for purge and trap.

<sup>e</sup> Use Method 5035 for purge and trap.

<sup>f</sup> Diesel analysis does not require acidification; however, acidified samples can be analyzed for diesel.

**Data Calculations and Reporting Units:**

Calculate the sample results using calibration factors determined according to Sections 7.7.2 of Method 8015B and 7.4.2 and 7.8.1 of SW-846 Method 8000A.

Report water sample results in concentration units of milligrams per liter (mg/L). Report soil sample results on a dry-weight basis in milligrams per kilogram (mg/kg).

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

**TABLE 1B. Target Compound List and Contract Required Detection Limits (CRQL) for SW-846 Method 8015B**

COMPOUND	CRQL Water mg/L	CRQL Soil mg/kg
Gasoline - Purge and Trap	0.5	10
Gasoline - Headspace	5.0	5
Diesel	0.5	10

Table 2. Summary of Calibration Procedures for Total Petroleum Hydrocarbons (TPH) as Gasoline and Diesel by SW-846 Method 8015B

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points for each analyte) (ICAL) <sup>a, b, c</sup>	Initially; whenever required, due to failure of CCV	RSD for CFs #20%; or, if using a linear calibration curve, a correlation coefficient ( <i>r</i> ) of 0.99 for each compound	1. Terminate analysis 2. Re-calibrate and verify before sample analysis
Continuing Calibration Verification (CCV) at midpoint of ICAL	Beginning of each 12 hour time period, after every 10 samples and end of run	%D between calculated amount and nominal amount within ±25%	1. Re-calibrate and verify good CCV 2. Re-analyze samples back to last good CCV
Retention time evaluation CCV standards	Each analysis of CCV standards	±3 x the SD of the avg ICAL RT for surrogate, See footnote <sup>c</sup> for GRO and DRO	1. Re-calibrate and verify good IPC 2. Re-analyze samples back to last good IPC

<sup>a</sup> The ICAL low standard must be above but near the CRQL. The low ICAL standard must have a signal to noise ratio \$5:1. If this requirement cannot be met, the laboratory must submit a MDL study as part of the data package.

<sup>b</sup> Gasoline Range Organics (GRO): C<sub>6</sub>-C<sub>10</sub>; Diesel Range Organics (DRO): C<sub>10</sub>-C<sub>28</sub>

<sup>c</sup> Establish and report retention time (RT) windows for GRO and DRO as described in Section 7.4 of Method 8015B and 7.6 of Method 8000B. Calculate RT windows for GRO and DRO based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component. Determine RT windows for surrogate compounds as ±3 x the standard deviation (SD) of the average ICAL RT for each analyte.

Table 3. Summary of Internal Quality Control Procedures for Total Petroleum Hydrocarbons (TPH) as Gasoline and Diesel by SW-846 Method 8015B

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	<u>Gasoline</u> : One per each 12 hour time period and after unusually concentrated samples <u>Diesel</u> : One per Batch or SDG <sup>a</sup> (1 per 20 samples minimum) and for each instrument used	< CRQL for each compound	1. Investigate source of contamination and document corrective action measures 2. Re-extract and re-analyze all samples processed with a method blank that is out-of-control
Surrogate Spike <sup>b</sup>	Every sample and MB at midpoint of calibration range	Water Samples: 75-125% of expected value Soil Samples: 60-125% of expected value	1. Re-analyze all samples with non-compliant surrogate recoveries
Matrix Sike and Matrix Spike Duplicate (MS/MSD)	One MS/MSD set per batch or SDG (1 MS/MSD set per 20 samples minimum)	65-135% of expected value; #30 RPD between MS and MSD	1. Report in case narrative
Laboratory Control Sample (LCS)	<u>Gasoline</u> : one each 12-hour period; <u>Diesel</u> : one per Batch or SDG	80-120% of expected value	1. Re-extract and re-analyze all samples processed with out-of-control LCS

<sup>a</sup> SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case;

Or each 14 calendar day period during which field samples in a case are received.

<sup>b</sup> Surrogates for GRO: 4-bromofluorobenzene and 1,1,1-trifluorotoluene;

Surrogate for DRO: hexacosane or ortho-terphenyl

Dilute and reanalyze samples with one or more analytes at concentrations exceeding the range of the calibration curve. Results for such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.



## ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS (PCBs)

SW-846 Method 8081 or 8080

**Table 1A. Summary of Holding Times and Preservation for Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)**

Analytical Parameter <sup>a</sup>	Technical and Contract Holding Times	Preservation
Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in Water Samples	<u>Technical for Extraction:</u> 7 days from collection;  <u>Contract for Extraction:</u> 5 days from receipt at laboratory  <u>Technical and Contract for Analysis:</u> 40 days from extraction	Cool to 4EC ±2EC
Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in Soil Samples	<u>Technical for Extraction:</u> 14 days from collection;  <u>Contract for Extraction:</u> 10 days from receipt at laboratory  <u>Technical and Contract for Analysis:</u> 40 days from extraction	Cool to 4EC ±2EC

<sup>a</sup> Individual target compounds are listed in Table 1B.**Data Calculations and Reporting Units:**

Calculate the calibration factors (CF) of single component pesticides according to Section 7.4.2 of SW-846 Method 8000A. Calculate sample results using the analyte CFs from the midpoint standard of the associated initial calibration curve. Perform sample quantitation for multiple components pesticides according to Section 7.6 of SW-846 Method 8080A or 8081.

Report water sample results in concentration units of micrograms per liter (Fg/L). Report soil sample results on a dry-weight basis in micrograms per kilogram (Fg/kg).

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

TABLE 1B. Target Compound List, CAS Numbers, and Contract Required Quantitation Limits (CRQL) for SW-846 Method 8081 or Method 8080

COMPOUND	CAS No.	CRQL Water µg/L	CRQL Soil µg/kg
alpha-BHC	319-84-6	0.05	2
beta-BHC	319-85-7	0.05	2
delta-BHC	319-86-8	0.05	2
gamma-BHC (Lindane)	58-89-9	0.05	2
Heptachlor	76-44-8	0.05	2
Aldrin	309-00-2	0.05	2
Heptachlor epoxide	1024-57-3	0.05	2
Endosulfan I	959-98-8	0.05	2
Dieldrin	60-57-1	0.1	3
4, 4'-DDE	72-55-9	0.1	3
Endrin	72-20-8	0.1	3
Endosulfan II	33213-65-9	0.1	3
4, 4'-DDD	72-54-8	0.1	3
Endosulfan sulfate	1031-07-8	0.1	3
4, 4'-DDT	50-29-3	0.1	3
Methoxychlor	72-43-5	0.5	17
Endrin ketone	53494-70-5	0.1	3
Endrin aldehyde	7421-93-4	0.1	3
alpha-Chlordane	5103-71-9	0.05	2
gamma-Chlordane	5103-74-2	0.05	2
Toxaphene	8001-35-2	5	170
Aroclor-1016	12674-11-2	1	33
Aroclor-1221	11104-28-2	2	67
Aroclor-1232	11141-16-5	1	33
Aroclor-1242	53469-21-9	1	33
Aroclor-1248	12672-29-6	1	33
Aroclor-1254	11097-69-1	1	33
Aroclor-1260	11096-82-5	1	3

**Table 2. Summary of Calibration Procedures for Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) by SW-846 Method 8081 or 8080**

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 3 points for each analyte) (ICAL) <sup>a,b,c</sup>	Initially; whenever required, due to failure of CCV	RSD for CFS #20% (#30% for Surrogate compounds)	1. Terminate analysis 2. Re-calibrate and verify before sample analysis
Continuing Calibration Verification (CCV) at midpoint of ICAL	Beginning of each day, after every 10 samples, and end of run	%D between CF of CCV and avg CFS from ICAL #25%	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV
Endrin and 4, 4'-DDT Breakdown	Beginning and end of analytical sequence	#20% each or #30% combined	1. Investigate source of the problem and document 2. If either Endrin, 4, 4'-DDT, or their breakdown products were detected, re-analyze the samples

<sup>a</sup> The ICAL low standard must be above but near the CRQL. The low ICAL standard must have a signal to noise ratio \$5:1. If this requirement cannot be met, the laboratory must submit a MDL study as part of the data package.

<sup>b</sup> ICAL Prepare initial calibration individual standard mixtures A and B (IND A and IND B) containing the single component pesticides specified in Table 9 of SW-846 Method 8081 at three concentration levels. For multiple response pesticides, including toxaphene and Aroclors (except 1016 and 1260), prepare separate initial calibration standards at the following concentration levels: Aroclors (except 1221) at 100 ng/mL; Aroclor-1221 at 200 ng/mL; and toxaphene at 500 ng/mL. Aroclor-1016 and Aroclor-1260 may be combined into a single standard solution. Spike all calibration standards with the surrogate compounds discussed in Table 3 at a concentration of 20 ng/mL.

<sup>c</sup> Report the retention time window for 5 major peaks from the initial calibration standard analysis.

Determine retention time windows for both single and multiple component pesticides using the following Guidelines:

Column Type      Retention Time Window  
                        in Minutes

Packed Column

# ± 2%

Mega bore or wide  
bore capillary column

① ±0.05 for tetrachloro-m-Xylene through Aldrin  
② ±0.07 for compounds which elute after Aldrin  
③ ±0.1 for decachlorobiphenyl

**Table 3. Summary of Internal Quality Control Procedures for Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) by SW-846 Method 8081 or 8080**

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per Batch or SDG <sup>a</sup> (1 per 20 samples minimum)	< CRQL for each compound	1. Investigate source of contamination and document 2. Re-extract and re-analyze all samples processed with a non-compliant method blank
Surrogate <sup>b</sup>	Every standard, sample, method blank and QC sample at 10 times CRQL	60-150% of expected value	1. Re-analyze all samples with non-compliant surrogate recoveries
Matrix Spike and Matrix Spike Duplicate (MS/MSD) <sup>c</sup>	One MS/MSD set per batch or SDG (1 MS/MSD set per 20 samples minimum)	50-135% of expected value; #30 RPD between MS and MSD	1. Address in narrative

<sup>a</sup> SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

<sup>b</sup> Spike each standard, sample, and blank with 1mL of a solution containing 0.2 Fg/mL each of tetrachloro-m-xylene and decachlorobiphenyl

<sup>c</sup> Spike MS/MSD samples with 1mL of a solution containing the following compounds and levels:

Target compound	Concentration (Fg/mL)	Target compound	Concentration (Fg/mL)
2-BHC	0.5	Heptachlor	0.5
4,4'-DDT	1.0	Aldrin	0.5
Endrin	1.0	Dieldrin	1.0

Dilute and re-analyze samples with one or more analytes at concentrations exceeding the range of the calibration curve. Results for such re-analyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

Second column confirmation is required for all positive results. Perform confirmation analyses on a column of a phase different from that used for quantitation. Confirmation analyses must meet all instrument calibration criteria and blank acceptance criteria specified in Table 2, above.



ORGANOPHOSPHORUS PESTICIDES

SW-846 Method 8141A

**Table 1A. Summary of Holding Times and Preservation for Organophosphorus Pesticides**

Analytical Parameter <sup>a</sup>	Technical and Contract Holding Times	Preservation
Organophosphorus Pesticides in Water	<u>Technical for Extraction:</u> 7 days from collection; <u>Contract for Extraction:</u> 5 days from receipt at laboratory  <u>Technical and Contract for Analysis:</u> 40 days from extraction	Cool to 4EC ±2EC;
Organophosphorus Pesticides in Soil	<u>Technical for Extraction:</u> 14 days from collection; <u>Contract for Extraction:</u> 10 days from receipt at laboratory  <u>Technical and Contract for Analysis:</u> 40 days from extraction	Cool to 4EC ±2EC;

<sup>a</sup> Target Compound List is provided in Table 1B

**Data Calculations and Reporting Units:**

Calculate the sample results using calibration factors determined according to Sections 7.4.2 and 7.8.1 of SW-846 Method 8000A.

Report water sample results in concentration units of micrograms per liter (Fg/L). Report soil sample results on a dry-weight basis in micrograms per kilogram (Fg/kg).

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

**TABLE 1B. Target Compound List, CAS Numbers, and Contract Required Quantitation Limits for Organophosphorus Pesticides SW-846 Method 8141**

Compound	CAS Number	CRQL Water ( $\mu\text{g}/\text{L}$ )	CRQL Soil ( $\mu\text{g}/\text{Kg}$ )
Azinphos methyl	86-50-0	1.0	50.0
Bolstar (Sulprofos)	35400-43-2	0.7	35.0
Chlorpyrifos	2921-88-2	0.7	50.0
Coumaphos	56-72-4	2.0	100.0
Demeton, O,S	8065-48-3	1.2	60.0
Diazinon	333-41-5	2.0	100.0
Dichlorvos	62-73-7	8.0	400.0
Dimethoate	60-51-5	2.6	130.0
Disulfoton	298-04-4	0.7	35.0
EPN	2104-64-5	0.4	20.0
Ethoprop	13194-48-4	2.0	100.0
Fensulfothion	115-90-2	0.8	40.0
Fenthion	55-38-9	0.8	50.0
Malathion	121-75-5	1.1	55.0
Merphos	150-50-5	2.0	100.0
Mevinphos	7786-34-7	5.0	250.0
Monocrotophos	6923-22-4	ND	ND
Naled	300-76-5	5.0	250.0
Parathion-ethyl	56-38-2	0.6	30.0
Parathion-methyl	298-00-0	1.2	60.0
Phorate	298-02-2	0.4	20.0
Ronnel	299-84-3	0.7	35.0
Sulfotep	3689-24-5	0.7	35.0
TEPP	21646-99-1	8.0	400.0
Stirophos (Tetrachlorovinsphos)	22248-79-9	8.0	400.0
Tokuthion (Protiothifos)	34643-46-4	0.7	55.0
Trichloronate	327-98-0	8.0	400.0

ND - Not Determined

**Table 2. Summary of Calibration Procedures for Organophosphorus Pesticides by SW-846 Method 8141**

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points for each analyte) (ICAL) <sup>a, b, c</sup>	Initially; whenever required, due to failure of CCV	RSD for CFS #20%;	1. Terminate analysis 2. Re-calibrate and verify before sample analysis
Continuing Calibration Verification (CCV) at midpoint of ICAL (Separate source from ICAL standards)	Following ICV and before sample analysis; after every 10 samples and end of run	%D between CF of CCV and avg CFS from ICAL #15%	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV
Retention time evaluation for CCV standards	Each analysis of CCV standards	$\pm 3 \times$ the SD of the avg ICAL RT for each analyte	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV

<sup>a</sup> The ICAL low standard must be above but near the CRQL. The low ICAL standard must have a signal to noise ratio \$5:1. If this requirement cannot be met, the laboratory must submit a MDL study as part of the data package.

<sup>b</sup> Report the retention time window for each analyte. Determine retention time windows as  $\pm 3 \times$  the standard deviation of the average initial calibration retention time for each analyte.

<sup>c</sup> ICAL and continuing CAL standards must contain all target analytes listed in Table 1B.

**Table 3. Summary of Internal Quality Control Procedures for Organophosphorus Pesticides by SW-846 Method 8141**

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per Batch or SDG <sup>a</sup> (1 per 20 samples minimum)	< CRQL for each compound	<ol style="list-style-type: none"> <li>Investigate source of contamination and document</li> <li>All samples processed with a method blank that is out of control must be re-extracted and re-analyzed</li> </ol>
Surrogate Spike	Every standard, sample and method blank at 10 times CRQL	<u>Water:</u> 75-125% of expected value <u>Soil:</u> 65-135% of expected value	<ol style="list-style-type: none"> <li>Re-analyze all samples with non-compliant surrogate recoveries</li> </ol>
Matrix Spike and Matrix Spike Duplicate (MS/MSD)	One MS/MSD set per batch or SDG (1 MS/MSD set per 20 samples minimum) containing a minimum of 5 of the analytes chosen from Table 1B	65-135% of expected value; #30 RPD between MS and MSD	<ol style="list-style-type: none"> <li>Address in Case Narrative</li> </ol>

<sup>a</sup> SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

Dilute and re-analyze samples with concentrations exceeding the range of the calibration curve. Results for such re-analyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

Second column confirmation is required for all positive results. Confirmation must be performed on a column of a phase different from that used for quantitation. Confirmation analyses must meet all calibration criteria specified in Table 2 and blank acceptance criteria specified in Table 3.



**CHLORINATED HERBICIDES**  
 SW-846 Method 8151,  
 Revision 0 (September 1994)

**Table 1A. Summary of Holding Times and Preservation for Chlorinated Herbicides**

Analytical Parameter <sup>a</sup>	Technical and Contract Holding Times	Preservation
Chlorinated Herbicides in Water	<u>Technical to Extraction:</u> 7 days from collection; <u>Contract to Extraction:</u> 5 days from receipt at laboratory  <u>Technical and Contract to Analysis:</u> 40 days from extraction	Cool to 4EC ±2EC;
Chlorinated Herbicides in Soil	<u>Technical to Extraction:</u> 14 days from collection; <u>Contract to Extraction:</u> 10 days from receipt at laboratory  <u>Technical and Contract to Analysis:</u> 40 days from extraction	Cool to 4EC ±2EC;

<sup>a</sup> Target Compound List is provided in Table 1B

**Data Calculations and Reporting Units:**

Calculate the sample results using calibration factors determined according to Sections 7.4.2 and 7.8.1 of SW-846 Method 8000A.

Report water sample results in concentration units of micrograms per liter (Fg/L). Report soil sample results on a dry-weight basis in micrograms per kilogram (Fg/kg).

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

**TABLE 1B. Target Compound List, CAS Numbers, and Contract Required Quantitation Limits for Chlorinated Herbicides SW-846 Method 8151**

<u>Compound</u>	<u>CAS Number</u>	<u>Water (ug/L)</u>	<u>Soil (ug/Kg)</u>
2,4-D	94-75-7	1.0	33
2,4-DB	94-82-6	1.0	33
2,4,5-T	93-76-5	1.0	33
2,4,5-TP (Silvex)	93-72-1	1.0	33
Dalapon	75-99-0	1.0	33
Dicamba	1918-00-9	1.0	33
Dichlorprop	120-36-5	1.0	33
Dinoseb	88-85-7	1.0	33
MCPP	93-65-2	500	17000
MCPA	94-74-6	500	17000

Table 2. Summary of Calibration Procedures for Chlorinated Herbicides by SW-846 Method 8151

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points for each analyte) (ICAL) <sup>a, b, c</sup>	Initially; whenever required, due to failure of CCV	RSD for CFS #20%; or, if using a linear calibration curve, a correlation coefficient ( <i>r</i> ) of 0.99 for each compound	1. Terminate analysis 2. Re-calibrate and verify before sample analysis
Continuing Calibration Verification (CCV) at midpoint of ICAL (Separate source from ICAL standards)	Beginning of each 12-hour time period, after every 10 samples and end of run	%D between calculated and nominal amount for each compound must be between $\pm 25.0\%$	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV
Retention time evaluation for CCV standards	Each analysis of CCV standards	$\pm 3 \times$ the SD of the avg ICAL RT for each analyte	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV

<sup>a</sup> The ICAL low standard must be above but near the CRQL. The low ICAL standard must have a signal to noise ratio  $\geq 5:1$ . If this requirement cannot be met, the laboratory must submit a MDL study as part of the data package.

<sup>b</sup> Report the retention time window for each analyte. Determine retention time windows as  $\pm 3 \times$  the standard deviation (SD) of the average initial calibration retention time for each analyte.

<sup>c</sup> ICAL and continuing CAL standards must contain all surrogate compounds and target analytes listed in Table 1B.

**Table 3. Summary of Internal Quality Control Procedures for Chlorinated Herbicides by SW-846 Method 8151**

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per Batch or SDG <sup>a</sup> (1 per 20 samples minimum) per analytical instrument	< CRQL for each compound	1. Investigate source of contamination and document 2. All samples processed with a method blank that is out of control must be re-extracted and re-analyzed
Surrogate Spike	Every standard, sample and method blank at 10 times CRQL	Water: 75-125% of expected value Soil: 65-135% of expected value	1. Re-analyze all samples with non-compliant surrogates recoveries 2. If re-analysis does not solve the problem, re-extract and re-analyze
Matrix Spike and Matrix Spike Duplicate (MS/MSD)	One MS/MSD set per batch or SDG (1 MS/MSD set per 20 samples minimum) containing a minimum of 5 of the analytes chosen from Table 1B	40-160% of expected value for dinoseb and 65-135% of expected value for other target analytes; #30 RPD between MS and MSD	1. Report in Case Narrative
Laboratory Control Sample (LCS)	One LCS per batch or SDG	40-160% for dinoseb; 80-120% for other target analytes	1. Re-extract and re-analyze all samples processed with an out-of-control LCS

<sup>a</sup> SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

Dilute and re-analyze samples with concentrations exceeding the range of the calibration curve. Results for such re-analyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

Second column confirmation is required for all positive results. Confirmation must be performed on a column of a phase different from that used for quantitation. Confirmation analyses must meet all calibration criteria specified in Table 2 and blank acceptance criteria specified in Table 3.